



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C02F 1/50, A01N 33/02, C08L 39/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/34834</b> <b>(43) International Publication Date:</b> 25 September 1997 (25.09.97)
<b>(21) International Application Number:</b> PCT/US97/04129 <b>(22) International Filing Date:</b> 18 March 1997 (18.03.97)  <b>(30) Priority Data:</b> 60/013,555                      18 March 1996 (18.03.96)                      US 08/732,131                      18 October 1996 (18.10.96)                      US  <b>(71) Applicant:</b> BIO-LAB, INC. [US/US]; 627 East College Avenue, P.O. Box 1489, Decatur, GA 30031-1489 (US).  <b>(72) Inventors:</b> BROWN, Geoffrey, A.; 5687 Hunters Crossing Ford, Lithonia, GA 30038 (US). MILLER, James, J.; 5940 Magnolia Mill Court, Norcross, GA 30092 (US). LINES, Ellwood, LeRoy, Jr.; 5630 Eden Roc Lane, Atlanta, GA 30342 (US). SHELOR, Susan, M.; 6280 Murets Road, Alpharetta, GA 30202 (US).  <b>(74) Agents:</b> THOMAS, Timothy, N. et al.; Woodard, Emhardt, Naughton, Moriarty & McNett, Bank One Center/Tower, Suite 3700, 111 Monument Circle, Indianapolis, IN 46204 (US).		<b>(81) Designated States:</b> AU, BR, CA, JP, MX, NZ, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> WATER CLARIFYING COMPOSITIONS  <b>(57) Abstract</b>  <p>Water clarifying compositions which are blends of one or more polymeric cation compounds and hydrogen peroxide. The polymeric cations are preferably polyquaternary ammonium compounds such as Q6/6, Q12/6, Q4/6 or PDED, or a cationic polymer such as PHMB. Combinations of two or more immiscible polymers may be preblended with concentrated hydrogen peroxide to provide shelf-stable, preblended compositions that may be applied as a single-dose product.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## WATER CLARIFYING COMPOSITIONS

### FIELD OF THE INVENTION

The present invention relates generally to water clarifying compositions, and more particularly to water clarifying compositions comprising combinations of two or more polymeric or non-polymeric non-oxidizing water treatment compositions.

### BACKGROUND OF THE INVENTION

The clarity of recreational waters is an important aspect of overall water quality. This is especially true in residential and commercial swimming pool applications where the clarity of the water indicates to the swimmer that the water is clean and pure.

Unfortunately, water can become cloudy as microorganisms (from the environment and swimmers), airborne particles and swimmer wastes accumulate, overwhelming the system's filtering capacity. When that happens, oxidizers such as chlorine, bromine, hydrogen peroxide and potassium peroxymonopersulfate are routinely used to achieve and maintain clean water. These oxidizers are typically added as solid, slow-release formulations, powders or liquids that achieve a desired level of oxidizer concentration.

There are, however, well-known drawbacks to using conventional oxidizers to clarify swimming pool water. For example, chlorine and bromine levels must be maintained at levels of 1-3 ppm and 4-6 ppm, respectively. Moreover, periodic superchlorination or superbromination is usually required to assure microbiological control and adequate

-2-

water quality. Hydrogen peroxide and potassium peroxymonopersulfate must be used in much higher concentrations because they are weaker oxidizers than the halogens (chlorine and bromine). Further, any oxidizer will  
5 cause bather irritation if the levels are too high.

Nonoxidizing antimicrobials such as polyquaternary ammonium compounds and PHMB are also known to be effective for controlling biofouling in various circulating water systems. For example, polyquats such as Q6/6 and PDED are  
10 important microbiocides and are widely used in water treatment.

Nonoxidizing antimicrobials are not, however, known to be effective clarifiers. Although PDED and PHMB have demonstrated some clarification properties under certain  
15 conditions, they are used primarily as antimicrobials in water treatment applications. The clarification that has been observed with these compositions has been attributed to the death of biofouling microbes and does not involve water that was repeatedly challenged by swimmer wastes.

It is also known that nonoxidizing biocides may sometimes be used in combination with other nonoxidizers to more effectively deal with the great diversity of microbial populations. From the perspective of antimicrobial performance, using combinations of biocides in tandem  
20 decreases the ability of microorganisms to adapt, since microbial adaptation to individual biocides is not uncommon.

Another important reason for using two antimicrobials simultaneously is to take advantage of synergistic effects. That is, some biocides have been shown to be more effective  
30 when combined with other antimicrobials. Even if there are no biocidally synergistic interactions, one compound may act as a non lethal adjuvant or potentiator for another. Although it would be desirable to apply products such as these in a single formulation, this may not be possible due  
35 to inherent blending incompatibilities. That is, the compounds of interest may not be miscible.

-3-

5 A need therefore exists for shelf-stable, preblended water clarifying compositions, and for compositions that increase the effective life of swimming pool oxidizers. A need also exists for water treatment compositions that are preblended combinations of two or more immiscible polyquaternary amonium compounds. The present invention addresses those needs.

-4-

## SUMMARY OF THE INVENTION

Briefly describing one aspect of the present invention, two or more polymeric or non-polymeric non-oxidizing agents are blended with hydrogen peroxide to make shelf-stable, water clarifying concentrates. In some preferred embodiments, non-oxidizing polymers such as polyquaternary ammonium compounds such as poly[hexamethylenedimethyl ammonium] chloride (Q6/6), Q12/6 (a homolog of Q6/6), Q4/6 (another homolog of Q6/6), PDED and IPCP are combined to make preblended water treatment concentrates. Non-polymeric, non-oxidizing compositions such as ADBAC, DDAC, DIDAC, DDC and DGH may also be used in the preblended concentrates.

In another aspect of the invention two or more immiscible polymeric compounds are combined in one preblended composition by using concentrated hydrogen peroxide as a formulating aid.

One advantage of the present invention is the provision of improved water clarifying compositions.

Another advantage of the present invention is the provision of compositions that increase the effective life of swimming pool oxidizers.

A third advantage of the present invention is the ability to combine two or more previously incompatible polymeric compounds into one preblended water treatment composition.

Further aspects and advantages of the present invention will be apparent from the following description.

-5-

## DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a tank apparatus as used in the examples.

FIG. 2 is a graph showing the effect of polymer on  $\text{H}_2\text{O}_2$ .

-6-

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

For the purpose of promoting an understanding of the principles of the invention, reference will now be made to preferred embodiments and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations and further modifications in the illustrated device, and such further applications of the principles of the invention as illustrated therein being contemplated as would normally occur to one skilled in the art to which the invention relates.

As previously described, one aspect of the present invention deals with the non-biocidal properties of cationic polymers in aqueous systems, and specifically with their ability to enhance water quality. In particular, the present invention relates to water enhancement including water clarification and/or reducing the amount of oxidizer demand present in aqueous systems. These phenomena have previously not been observed with monomeric cations (e.g., monomeric quaternary ammonium salts).

In addition, one aspect of the present invention provides a method of formulating preblended liquid concentrates for treating water with a combination of polymeric or non-polymeric compounds. Surprisingly, combinations of water treatment agents that are immiscible when blended alone may be preblended to make effective water treatment concentrates when formulated with concentrated hydrogen peroxide.

Further describing one aspect of the present invention, there are provided synergistic combinations of cationic polymers (such as Q6/6, PHMB and PDED) and oxidizers (such as  $H_2O_2$  and chlorine) for use in clarifying swimming pool waters. It can be seen from the following data that the compositions of the present invention work far better



-7-

for clarifying water than either polyquats or oxidizers acting alone.

The polymeric cations of one aspect of the present invention include polyquaternary ammonium compounds (polyquats) such as 1,6-hexanediamine-N,N,N',N'-tetramethyl polymer with 1,6-dichlorohexane (Q6/6, also identified as poly[hexamethylenedimethyl ammonium] chloride) and two of its homologs (Q12/6 and Q4/6). These compounds are known to the art and may be prepared as described, for example, in U.S. Patent No. 5,142,002 to Metzner. In addition, the polyquaternary ammonium compound poly[oxyethylene-(dimethylimino) ethylene-(dimethylimino) ethylene dichloride] (PDED) or polycations such as poly(iminoimidocarbonyl-iminoimidocarbonyliminohexamethylene) chloride (also called polyhexamethylene biguanide or PHMB) may be used.

For the purposes of this disclosure, the term "oxidizer" is defined consistent with the use of that term by persons of ordinary skill in the art of swimming pool water treatment. Oxidizers useful in the synergistic compositions of the present invention include chlorine, bromine,  $H_2O_2$ , and other oxygen-releasing oxidizers.

In another aspect of the invention concentrated hydrogen peroxide is used as a formulating agent for concentrated, miscible or immiscible mixtures of polymeric or non-polymeric compounds such as polymeric quaternary ammonium compounds (polyquats), monomeric, dimeric or oligomeric quaternary ammonium compounds (quats), etc. More particularly, compounds such as poly(hexamethylammonium) chloride (Q6/6), isomers of Q6/6 (particularly, Q12/6 and Q4/6), poly[oxyethylene (dimethylimino) ethylene-(dimethylimino) ethylene] dichloride (PDED), dodecamethylene-dimethylimino chloride (Q6/12), 1,3-diazo-2,4-cyclopentadiene with 1-chloro-2,3-epoxypropane (IPCP), dodecylguanidine hydrochloride (DGH),

-8-

diisodecyldimethyl ammonium chloride (DDC),  
alkyldimethylammonium chloride (ADBAC),  
N-decyl-N-isononyl-N,N-dimethylammonium chloride (DIDAC) and  
didecyldimethyl ammonium chloride (DDAC) are examples of  
5 compounds that are preferably formulated with hydrogen  
peroxide as disclosed and claimed in this aspect of the  
present invention.

Reference will now be made to specific examples using  
the processes described above. It is to be understood that  
10 the examples are provided to more completely describe  
preferred embodiments, and that no limitation to the scope  
of the invention is intended thereby.

#### EXAMPLES

Experimental Setup. Microbes such as Pseudomonas  
15 aeruginosa, Escherichia coli, and Staphylococcus aureus are  
some of the major bacteria which can be recovered from  
recreational waters after swimmer use. Mixtures of these  
bacteria (ca.  $10^{10}$  -  $10^{11}$  organisms) were added to 10  
gallon tanks containing balanced pool water (200 ppm calcium  
20 carbonate, 120 ppm calcium sulfate, pH 7.4). In addition,  
10 ml of a synthetic insult was added to each aquarium at  
the time of inoculation.

The synthetic insult used in the following examples was  
composed of:

25	<u>Components</u>	<u>g/L</u>
	NaCl	40.0
	K <sub>2</sub> SO	4.0
	Na <sub>2</sub> SO <sub>4</sub>	0.8
	MgSO <sub>4</sub>	8.0
30	CaCl <sub>2</sub>	0.56
	Dextrose	1.2
	Lactid Acid	8.0
	Pyruvic Acid	0.4
	Urea	29.2
35	Creatinine	1.6

An attached pump and filter assured adequate mixing.

-9-

The filter contained a 4 x 7 inch section from a standard pool cartridge filter inside a porous housing. See Fig. 1. Three tanks were used for each experiment.

#### EXAMPLE 1

Experiment 1 was performed to determine the water clarification potential of low doses of conventional oxidizers. Four ten-gallon tanks were filled with balanced pool water. Tanks 1 and 2 contained no oxidizer. Tanks 3 and 4 contained  $H_2O_2$  and chlorine, respectively.

Oxidizer was added daily to achieve a desired oxidizer concentration.

Pieces of compressed oxidizer were placed into the water intake tube of the pump. Dissolved oxidizer traveled through the pump and filter assembly and then into the bulk water. Skimmer fed oxidizer is applied this way in actual pools. After achieving the desired residual oxidizer level, bacteria were added to tanks 2, 3 and 4. Tank 1 was the only tank which received neither bacteria nor oxidizer.

Table 1 shows the results of experiment 1. It can be seen from Table 1 that low levels of chlorine or  $H_2O_2$  had no demonstrable effect on water clarity.

Table 1. Clarifying Effect Of Oxidizer Only.

TANK	DAY	OXIDIZER PPM	TURBIDITY (NTU)
1	1	-	0
	2	-	0.12
	3	-	0.17
2	1	-	1.36
	2	-	2.15
	3	-	3.55
3	1	6.8	1.43
	2	2.72	3.10
	3	1.53	4.47
4	1	0.43	1.43
	2	0.50	2.08
	3	0.43	2.82

-10-

## EXAMPLES 2-4

Experiments 2-4 were performed to demonstrate the effects of polymeric cations (such as polyquaternary ammonium compounds) and chlorine on water quality. Two  
5 ten-gallon tanks were dosed with about 5 ppm of either Q6/6, Q12/6, Q4/6 or PDED. One of these tanks and the third tank was treated with low levels of chlorine. Pieces of compressed chlorine (trichloroisocyanurate) were placed into the water intake tube of the pump. Dissolved chlorine  
10 traveled through the pump and filter and then into the bulk water, as typically applied in swimming pools.

Chlorine levels were measured by titration with 0.1 N sodium thiosulfate. After achieving a chlorine residual of ca. 0.5 ppm (usually no higher than 1 ppm) or less, bacteria  
15 were added.

Tables 2-4 show the synergistic effect that chlorine and polyquats have on water quality. In each of the tables, tank #1 was dosed with compressed trichloroisocyanurate for successive days, tank #2 was dosed with ca. 5 ppm of  
20 cationic polymer and tank #3 contained a mixture of chlorine and cationic polymer. Bacteria were added each day. The amount of bacteria added was sufficient to give the water a cloudy appearance.

Water turbidity (NTU) was initially measured after about  
25 3 hours, and was measured daily thereafter. After the first

-11-

inoculation (Day 1), tank #1 required twice as long as tank #3 to reach a comparable chlorine residual.

Water turbidity was high after the first inoculation and increased with subsequent inoculations (tank #1). Tanks  
5 containing only polyquats were substantially clearer (tank #2). Tank #3 generally had the lowest turbidities. In actual pools, a turbidity reading of greater than 0.3 NTU is considered hazy.

Spot microbiological testing revealed no direct  
10 correlation between bacterial density and water clarity. In some cases, tanks with high turbidities showed low or no bacterial counts. By contrast, some of the least turbid tanks had the highest bacterial counts. Therefore,  
15 clarification can be seen to correlate specifically to the reduction in turbidity, and not necessarily to a reduction in the microbial population.

In all cases, the amounts of oxidizers used were too low to give adequate clarification after the first day.  
However, some combinations of oxidizers and polymers showed  
20 a synergistic effect upon clarification. All of the polymers enhanced water quality by decreasing the amount of oxidizer consumed by the system's demand. In this way, the overall effectiveness of the cationic polymers increased the effectiveness of the oxidizers by allowing them to remain  
25 active for longer periods of time.

-12-

Table 2 . Enhanced Chlorine:Q6/6 Clarifier.

TANK	DAY	PPM CL <sub>2</sub>	PPM Q6/6	TURBIDITY
1	1	0.35	-	0.56
	2	0.35	-	0.96
	3	0.35	-	1.6
2	1	-	6	0.1
	2	-	6	0.09
	3	-	6	0.32
3	1	0.35	6	0.08
	2	0.35	6	0.08
	3	0.53	6	0.12

Table 3 . Enhanced Chlorine:Q12/6 Clarifier.

TANK	DAY	PPM CL <sub>2</sub>	PPM Q12/6	TURBIDITY
1	1	0.39	-	0.51
	2	1.06	-	1.1
	3	0.71	-	4.5
2	1	-	5	0.24
	2	-	5	0.24
	3	-	5	0.27
3	1	0.35	5	0.28
	2	0.35	5	0.16
	3	0.53	5	0.13

Table 4 . Enhanced Chlorine: PDED Clarifier.

TANK	DAY	PPM CL <sub>2</sub>	PPM PDED	TURBIDITY
1	1	0.71	-	0.24
	2	0.71	-	0.46
	3	0.35	-	0.89
2	1	-	6	0.07
	2	-	6	0.09
	3	-	6	0.35
3	1	0.71	5	0.05
	2	0.85	5	0.05
	3	0.18	5	0.07

-13-

## EXAMPLES 5-9

Tables 5-8 show the effect of polycations upon hydrogen peroxide stability. Table 9 shows the effect of a cationic monomer, alkyldimethylammonium chloride (ADBAC), upon peroxide and water clarity.

In all cases, polymeric cations decreased the amount of oxidizer demand, extending the half life of the  $H_2O_2$ . However, Table 9 indicates that the beneficial effects that cations have on water quality may be limited to polymers. The monomeric cation did not extend the  $H_2O_2$  half life, and had little if any effect upon water clarity.

Table 8 demonstrates that the cationic polymer PHMB also showed clarification synergy with hydrogen peroxide. This proves that the synergistic effect between oxidizers and cationic polymers is not a property unique to polyquaternary ammonium compounds such as Q6/6 and PDED. PHMB was not tested in the presence of chlorine because it is not compatible with oxidizing halogens.

Table 5. Enhanced Peroxide:Q6/6 Clarifier.

TANK	DAY	PPM $H_2O_2$	PPM Q6/6	TURBIDITY
1	1	7.65	-	0.49
	2	4.25	-	1.3
	3	0.68	-	0.61
2	1	-	4	0.29
	2	-	4	0.15
	3	-	4	0.95
3	1	7.65	6	0.28
	2	5.61	6	0.13
	3	2.72	6	0.58

-14-

Table 6. Enhanced Peroxide: PDED Clarifier.

TANK	DAY	PPM $H_2O_2$	PPM PDED	TURBIDITY
1	1	8.16	-	0.42
	2	4.25	-	1.0
	3	0	-	0.40
2	1	-	5	0.43
	2	-	5	0.19
	3	-	5	0.68
3	1	8.5	6	0.24
	2	5.1	6	0.09
	3	1.7	6	0.57

Table 7. Enhanced Peroxide: Q12/6 Clarifier.

TANK	DAY	PPM $H_2O_2$	PPM Q12/6	TURBIDITY
1	1	7.65	-	0.54
	2	8.5	-	0.3
	3	2.55	-	1.6
2	1	-	4	0.27
	2	-	4	0.17
	3	-	4	0.22
3	1	7.65	6	0.3
	2	7.65	6	0.15
	3	5.10	6	0.28

Table 8. Enhanced Peroxide: PHMB Clarifier.

TANK	DAY	PPM $H_2O_2$	PPM PHMB	TURBIDITY
1	1	7.65	-	0.54
	2	8.5	-	0.8
	3	2.55	-	1.6
2	1	-	4	0.84
	2	-	4	0.61
	3	-	4	0.78
3	1	7.68	4	0.59
	2	8.5	4	0.37
	3	8.5	4	0.45



-15-

Table 9. Effect of ADBAC Quat on Water Clarity.

TANK	DAY	PPM $H_2O_2$	PPM ADBAC	TURBIDITY
1	1	6.8	-	0.83
	2	5.1	-	0.87
	3	1.7	-	1.1
2	1	-	4	0.44
	2	-	4	1.0
	3	-	4	1.5
3	1	7.65	4	0.5
	2	1.7	4	0.55
	3	1.7	4	1.8

## EXAMPLE 10

In another experiment, various cations (polymers and monomers) and  $H_2O_2$  were tested as clarifiers in cloudy water containing PHMB. Nine aquariums were dosed with 5 ppm of PHMB and inoculated on successive days with suspensions of *P. aeruginosa*, *E. coli*, *S. aureus* and synthetic sweat until the water remained cloudy for at least 18 hr. Cloudy water is a recalcitrant problem associated with PHMB sanitized pools.

The list of potential clarifiers included polycations (Q6/6, Q12/6, Q4/6, PDED and PHMB), the monomeric cation diisodecyl dimethyl ammonium chloride (DDAC) and  $H_2O_2$ . Each quat was dosed at 10 ppm along with 10 ppm  $H_2O_2$ . The results are recorded in Table 10.

The data in Table 10 indicate that mixtures of cationic polymers with low levels of  $H_2O_2$  can act as clarifiers in cloudy PHMB systems. By contrast, monomeric cations were unable to act as clarifiers under any circumstances (Tables 9 and 10).  $H_2O_2$  alone demonstrated clarification because its dose was tripled to roughly 30 ppm.

-16-

Table 10. Ability of Compounds to Clarify Cloudy Water.

COMPOUND	PPM ADDED	TURBIDITY	
		INITIAL	18 HR
CONTROL	0	2.2	2.4
Q6/6	10	1.2	0.8
Q12/6	10	1.0	0.6
PDED	10	1.6	0.52
DDAC	10	2.4	2.2
Q4/6	10	1.1	0.6
PHMB	10	1.2	0.52
H <sub>2</sub> O <sub>2</sub> <sup>1</sup>	10	1.7	1.0

<sup>1</sup> - A triple dose of H<sub>2</sub>O<sub>2</sub> was used (30 ppm), in lieu of the usual 10 ppm.

## EXAMPLE 11

The ability of polyquats to extend the life of oxidizers in non halogen systems was demonstrated by an outdoor experiment using actual swimmers. Two above-ground pools (5,000 gallons each) were treated with 10 ppm PHMB, 2 ppm ADBAC quat and 27 ppm of H<sub>2</sub>O<sub>2</sub>. Five parts per million of Q6/6 was added to one of the pools. Swimmers spent an average of 16 total hours (4 swimmers/pool, 2 hours each) per week in one pool. Hydrogen peroxide levels were monitored daily and are recorded in FIG. 2.

-17-

FIG. 2 shows that the pool with 5 ppm Q6/6 maintained consistently higher peroxide levels than the pool without any polyquat. Moreover, the pool without polyquat required greater and more frequent re-applications of  $H_2O_2$  than the pool with Q6/6. In spite of these larger peroxide additions, the pool without the additional cationic polymer was unable to achieve the  $H_2O_2$  levels found in the pool containing the polyquat (Fig. 2). This field research corroborates the extensive laboratory studies summarized in Tables 1-8.

Although the pool with the polyquat maintained higher  $H_2O_2$  levels, the laboratory data indicate that a pool utilizing a monomeric cation and peroxide would have had substantially lower  $H_2O_2$  levels than the PHMB pool without polyquat.

#### EXAMPLE 12

##### Determination of miscibility of polyquaternary amonium compounds.

In order to determine whether certain combinations of non-oxidizing compounds which may demonstrate biocidal or clarification synergy when used simultaneously could be blended together as concentrated products, a variety of useful polymeric water treatment agents were combined to determine their relative miscibilities. The Table below shows blends of several polymeric and non-polymeric compounds that are or might be commercially valuable as biocides, clarifiers or stabilizers in water treatment, hard surface sanitizers or consumer products. "M" and "I" denote miscible and immiscible, respectively.

-18-

TABLE: BLENDS OF POLYMERIC AND NON-POLYMERIC COMPOUNDS.

	Q6/6	Q6/12	PDED	IPCP	ADBAC	DDAC	DIDAC	DDC	DGH
Q6/6	M	I	M	M	I	I	I	I	I
Q6/12	I	M	I	M	M	I	I	I	M
5 PDED	M	I	M	M	I	I	I	I	I
IPCP	M	M	M	M	I	I	I	I	I
ADBAC	I	M	I	I	M	M	M	M	M
DDAC	I	I	I	I	M	M	M	M	M
DIDAC	I	I	I	I	M	M	M	M	M
10 DDC	I	I	I	I	M	M	M	M	M
DGH	I	M	I	I	M	M	M	M	M

Solutions of concentrated hydrogen peroxide (0.1-50%)  
 are blended with compounds that may or may not be readily  
 miscible. These non-oxidizing blends hold commercial value  
 15 for treating industrial or recreational regulated waters,  
 hard surface sanitization or for household consumer use.  
 The concentrated solutions are preferably applied as a  
 single product in waters or on hard surfaces. The

-19-

combinations of non-oxidizing compounds are preferably added to the peroxide in concentrations ranging from 0.1-10%.

#### EXAMPLE 13

##### Blends of immiscible polyquaternary amonium compounds.

5       The combination of Q6/6 and Q6/12 was determined to be immiscible when blended as concentrates. Concentrated (35%) hydrogen peroxide was used as a dissolution agent to prepare an aqueous Q6/6:Q6/12:hydrogen peroxide blend with a final  
10 formulation of about 5% Q6/6, about 5% Q6/12, and about 25% hydrogen peroxide. No phase separation occurred, and the concentrated water treatment product was observed to be shelf-stable for a period of at least about 60 days when stored at room temperature.

#### EXAMPLE 14

15       Blends of immiscible polymeric water treatment agents.

      The combination of PDED and Q6/12 was determined to be immiscible when blended as concentrates. Concentrated (35%) hydrogen peroxide was used as a dissolution agent to prepare an aqueous PDED:Q6/12:hydrogen peroxide blend with a final  
20 formulation of about 2% PDED, about 3% Q6/12, and about 30% hydrogen peroxide. No phase separation occurred, and the concentrated water treatment product was observed to be shelf-stable for a period of at least about 60 days when stored at room temperature.

-20-

## EXAMPLE 15

Blends of immiscible polymeric and non-polymeric water treatment compositions.

5 The combination of Q6/6, PDED and DIDAC was determined to be immiscible when blended as concentrates. Concentrated (35%) hydrogen peroxide was used as a dissolution agent to prepare an aqueous Q6/6:PDED:DIDAC:hydrogen peroxide blend with a final formulation of about 5% Q6/6, about 10% PDED, about 2% DIDAC and about 25% hydrogen peroxide. No phase  
10 separation occurred, and the concentrated product was observed to be shelf-stable for a period of at least about 60 days when stored at room temperature.

15 It can be seen from the above that hydrogen peroxide is an effective formulating agent for compounds such as those listed in the Table above. This list is not exhaustive however, and merely identifies representative examples of compounds which one skilled in the art might use in compositions formulated with hydrogen peroxide according to the present invention.

20

## EXAMPLE 16

Shelf-stable, preblended combinations of non-oxidizing cationic polymers and hydrogen peroxide.

25 Shelf-stable, preblended concentrates of Q6/6 and hydrogen peroxide are prepared by combining 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 95% portions of

-21-

concentrated hydrogen peroxide with 95%, 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20%, 10%, and 5% portions, respectively, of Q6/6 to make a liquid concentrate. The concentrates were observed to be shelf-stable for at least about 60 days when  
5 stored at room temperature.

## EXAMPLE 17

Shelf-stable, preblended combinations of non-oxidizing cationic polymers and hydrogen peroxide.

Shelf-stable, preblended concentrates of Q12/6 and  
10 hydrogen peroxide are prepared by combining 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 95% portions of concentrated hydrogen peroxide with 95%, 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20%, 10%, and 5% portions, respectively, of Q12/6 to make a liquid concentrate. The concentrates were  
15 observed to be shelf-stable for at least about 60 days when stored at room temperature.

## EXAMPLE 18

Shelf-stable, preblended combinations of non-oxidizing cationic polymers and hydrogen peroxide.

Shelf-stable, preblended concentrates of Q4/6 and  
20 hydrogen peroxide are prepared by combining 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 95% portions of concentrated hydrogen peroxide with 95%, 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20%, 10%, and 5% portions, respectively, of  
25 Q4/6 to make a liquid concentrate. The concentrates were observed to be shelf-stable for at least about 60 days when stored at room temperature.

-22-

## EXAMPLE 19

Shelf-stable, preblended combinations of non-oxidizing cationic polymers and hydrogen peroxide.

5 Shelf-stable, preblended concentrates of PDED and hydrogen peroxide are prepared by combining 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 95% portions of concentrated hydrogen peroxide with 95%, 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20%, 10%, and 5% portions, respectively, of PDED to make a liquid concentrate. The concentrates were  
10 observed to be shelf-stable for at least about 60 days when stored at room temperature.

15 While the invention has been illustrated and described in detail in the foregoing description, the same is to be considered as illustrative and not restrictive in character, it being understood that only the preferred embodiment has been shown and described and that all changes and modifications that come within the spirit of the invention are desired to be protected.



-23-

## CLAIMS

What is claimed is:

1. A preblended water clarifying composition, comprising:

- 5 (a) between about 5% and about 95% of a first cationic polymer;  
(b) between about 5% and about 95% of a second cationic polymer; and  
(c) between about 0.1% and about 50% of a concentrated hydrogen peroxide formulating agent.

10 2. A water clarifying composition according to claim 1 wherein at least one of said cationic polymers is a quaternary ammonium compound.

3. A water clarifying composition according to claim 2 wherein at least one of said polyquaternary ammonium  
15 compound is a member selected from the group consisting of poly(hexamethylammonium) chloride (Q6/6 or its isomers Q12/6 and Q4/6), poly [oxyethylene (dimethylimino) ethylene-(dimethylimino) ethylene] dichloride (PDED), dodecamethylene-dimethylimino chloride (Q6/12),  
20 1,3-diazo-2,4-cyclopentadiene with 1-chloro-2,3-epoxypropane (IPCP), dodecylguanidine hydrochloride (DGH), diisodecyldimethyl ammonium chloride (DDC), alkyl dimethyl ammonium chloride (ADBAC), N-decyl-N-isononyl-N,N-dimethyl ammonium chloride (DIDAC) and  
25 didecyldimethyl ammonium chloride (DDAC).

4. A method of clarifying water comprising adding to the water a clarifyingly effective amount of a composition comprising:

- (a) between about 5% and about 95% of a first

-24-

cationic polymer;

(b) between about 5% and about 95% of a second cationic polymer; and

(c) between about 0.1% and about 50% of a concentrated hydrogen peroxide formulating agent.

5        5.    A method according to claim 4 wherein at least one of said cationic polymers is a polyquaternary ammonium compound.

10        6.    A method according to claim 5 wherein said polyquaternary ammonium compound is a member selected from the group consisting of poly(hexamethylammonium) chloride (Q6/6 or its isomers Q12/6 and Q4/6), poly [oxyethylene (dimethylimino) ethylene-(dimethylimino) ethylene] dichloride (PDED), dodecamethylene-dimethylimino chloride (Q6/12), 1,3-diazo-2,4-cyclopentadiene with 1-chloro-2,3-epoxypropane (IPCP), dodecylguanidine hydrochloride (DGH), diisodecyldimethyl ammonium chloride (DDC), alkyldimethylammonium chloride (ADBAC), N-decyl-N-isononyl-N,N- dimethylammonium chloride (DIDAC) and didecyldimethyl ammonium chloride (DDAC).

7.    A water clarifying composition comprising a cationic polymer and an oxidizer.

25        8.    A water clarifying composition according to claim 7 wherein the cationic polymer is a quaternary ammonium compound.

9.    A water clarifying composition according to claim 8 wherein said polyquaternary ammonium compound is a member selected from the group consisting of Q6/6, Q12/6, Q4/6 and PDED.

-25-

10. A water clarifying composition according to claim 7 wherein said oxidizer is a halogen-containing oxidizer.

11. A water clarifying composition according to claim 7 wherein said oxidizer is an oxygen-releasing oxidizer.

5 12. A water clarifying composition according to claim 7 wherein said oxidizer is a member selected from the group consisting of  $H_2O_2$  and chlorine-containing compounds.

10 13. A water clarifying composition according to claim 8 wherein said polyquaternary ammonium compound is a member selected from the group consisting of Q6/6, Q12/6, Q4/6 and PDED, and said oxidizer is a member selected from the group consisting of  $H_2O_2$  and chlorine-containing compounds.

15 14. A water clarifying composition according to claim 8 wherein said water clarifying composition consists essentially of: (1) a polyquaternary ammonium compound selected from the group consisting of Q6/6, Q12/6, Q4/6 and PDED; and (2) an oxidizer selected from the group consisting of  $H_2O_2$  and chlorine-containing compounds.

20 15. A water clarifying composition according to claim 8 wherein said water clarifying composition consists essentially of: (1) a polyquaternary ammonium compound selected from the group consisting of Q6/6, Q12/6, Q4/6 and PDED; and (2)  $H_2O_2$ .

25 16. A water clarifying composition according to claim 8 wherein said water clarifying composition consists essentially of: (1) a polyquaternary ammonium compound selected from the group consisting of Q6/6, Q12/6, Q4/6 and PDED; and (2) a chlorine-containing compound.

-26-

17. A water clarifying composition according to claim 8 wherein said water clarifying composition consists essentially of Q6/6 and  $H_2O_2$ .

5 18. A water clarifying composition according to claim 8 wherein said water clarifying composition consists essentially of Q6/6 and a chlorine-containing compound.

19. A water clarifying composition according to claim 7 wherein the cationic polymer is polyhexamethylene biguanide (PHMB).

10 20. A method of clarifying water comprising adding to the water a clarifyingly effective amount of a shelf-stable, preblended composition comprising a cationic polymer and hydrogen peroxide.

15 21. A method according to claim 20 wherein said cationic polymer is a polyquaternary ammonium compound.

22. A method according to claim 21 wherein said polyquaternary ammonium compound is a member selected from the group consisting of Q6/6, Q12/6, Q4/6 and PDED.

20 23. A method according to claim 21 wherein said water clarifying composition consists essentially of: (1) a polyquaternary ammonium compound selected from the group consisting of Q6/6, Q12/6, Q4/6 and PDED; and (2)  $H_2O_2$ .

25 24. A method of clarifying used swimming pool water comprising adding a clarifyingly effective amount of a shelf-stable, preblended composition consisting essentially of a cationic polymer and a chlorine-containing compound to swimming pool water which includes bather sweat.

-27-

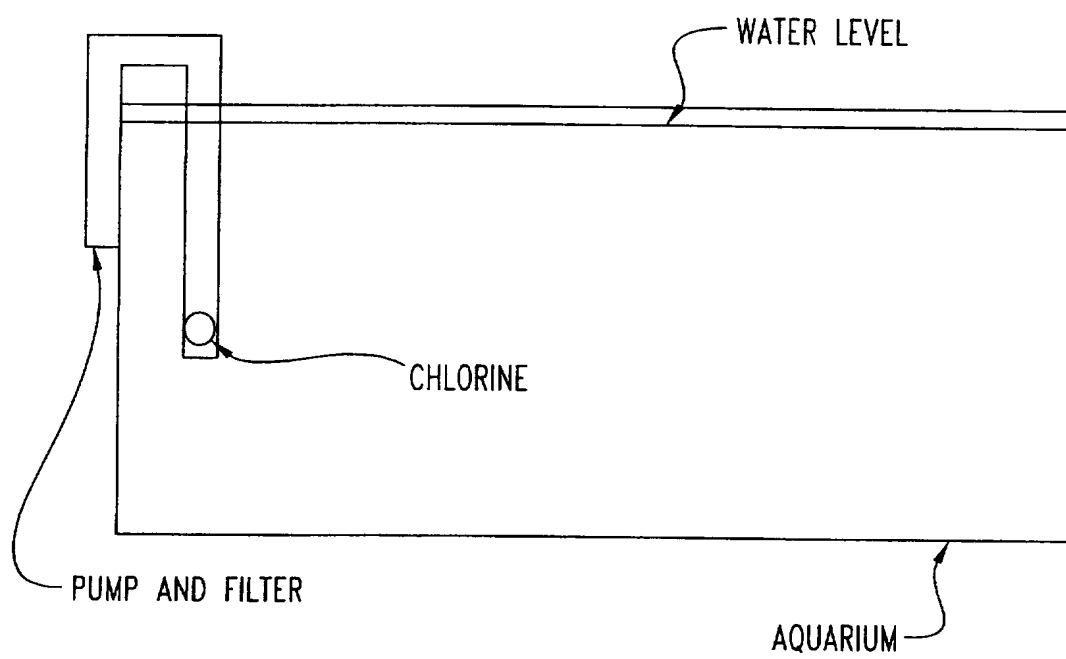
25. A method according to claim 24 wherein said cationic polymer is a polyquaternary ammonium compound.

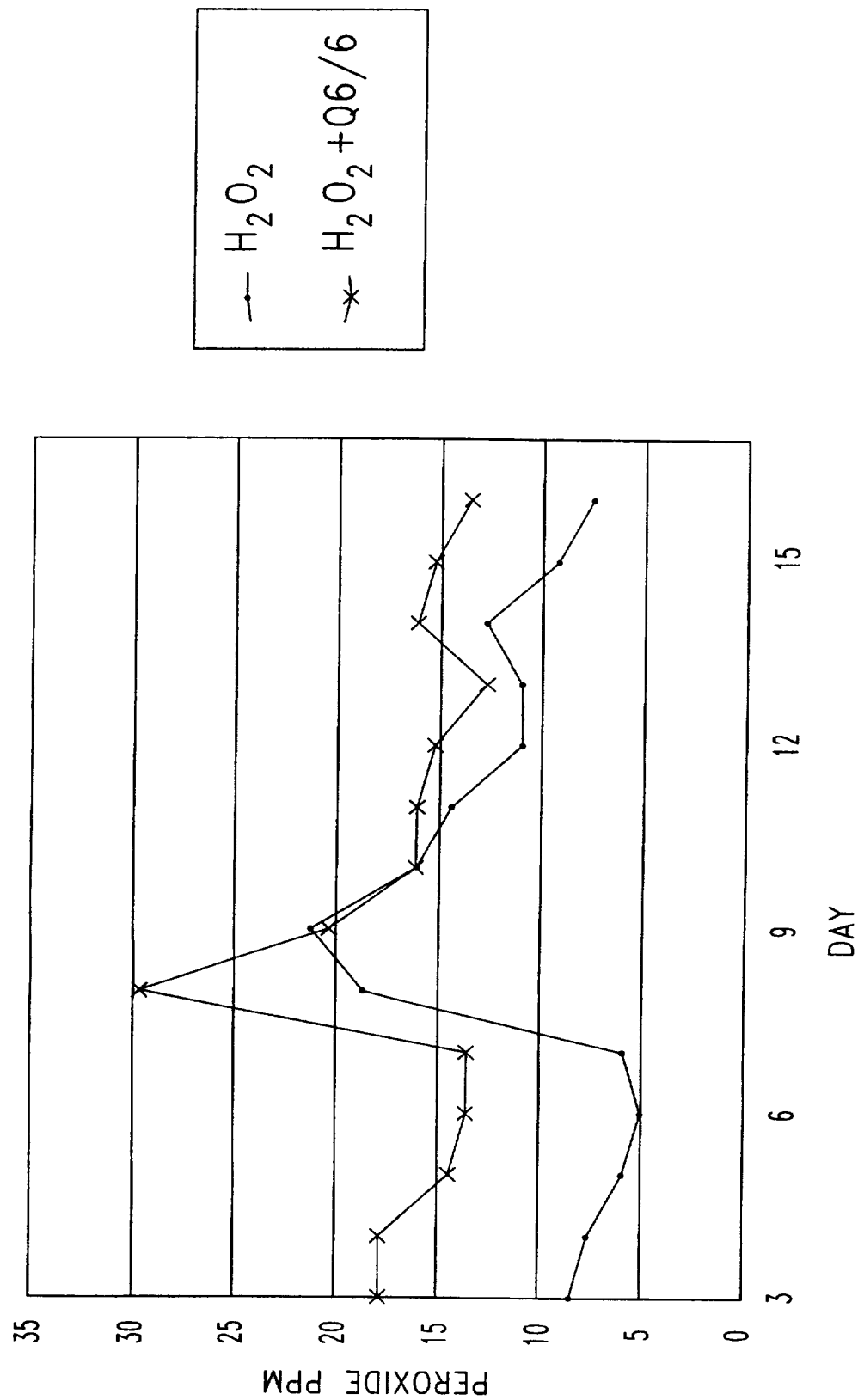
26. A method of increasing the effective life of hydrogen peroxide in swimming pool water, comprising  
5 providing the hydrogen peroxide to the pool as a shelf-stable, preblended composition consisting essentially of a cationic polymer and hydrogen peroxide.

27. A method according to claim 26 wherein said cationic polymer is a polyquaternary ammonium compound.

10 28. A method according to claim 27 wherein said polyquaternary ammonium compound is selected from the group consisting of Q6/6, Q12/6, Q4/6 and PDED.

29. A method according to claim 26 wherein said cationic polymer is polyhexamethylene biguanide (PHMB).

**Fig. 1**

**Fig. 2**

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/04129

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : C02F 1/50; A01N 33/02; C08L 39/00

US CL : 210/754, 759, 764; 523/122; 524/555

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 210/754, 759, 764; 523/122; 524/555

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS; quaternary ammonium, peroxide#, pool

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,654,208 A (STOCKEL et al) 31 March 1987, see col. 9, lines 34-39, col. 10, lines 45-64 and claim 1.	7, 8, 10-12, 19
X ---- Y	US 5,142,002 A (METZNER) 25 August 1992, see col. 3, lines 54-68, col. 4, lines 8-19, col. 5, lines 52-65, col. 6, table and col. 7, lines 50-52.	1-18, 20-28 ---- 19, 29
Y	US 5,449,658 A (UNHOCH et al) 12 September 1995, see abstract.	19, 29

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*&*	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

30 MAY 1997

Date of mailing of the international search report

24 JUN 1997

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

TAE H. YOON

Telephone No. (703) 308-2351